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HIGH GLASS-TRANSITION TEMPERATURE POLYMER NETWORKS HARNESSING THE DYNAMIC RING OPENING OF PINACOL BORONATES.

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KEYWORDS. [Boron chemistry, organoboron polymers, high glass-transition temperature, dynamic networks, reversible crosslinking]

ABSTRACT: Differential scanning calorimetry of high molar mass poly(4-vinylphenylboronic acid, pinacol ester)s evidenced unusual reactive events above 130°C, resulting in a high glass transition temperature of 220°C. We hypothesize a ring-opening reactivity of pinacol boronates involving a nucleophilic attack on the sp2 boron and subsequent bridging by interconnected pinacol moieties to form a densely cross-linked network with high-T_g. FTIR, solid-state NMR investigations and rheology studies on the polymer as well as double-tagging analyses on molecular model structures and theoretical calculations further support this hypothesis and indicate an entropy-driven ring-opening inducing crosslinking. When diluted in an apolar solvent such as toluene, the polymer network can be resolubilized *via* ring closing thus recovering the entropically-favoured linear chains featuring cyclic boronate esters. The introduction of boron reactivity in polymer chains may open a path to a new class of dynamic polymer networks with uncommon and exciting thermodynamics.

Polymers comprising boronic/boronate groups have been the focus of intensive research due to their unique properties associated with the electron deficiency of boron conferring reactivity harnessed

via post-polymerisation.[1,2] A wide variety of derivatisations through simple nucleophilic coordination at the boron vacancy enables versatile functionalisation and precise macromolecular engineering. To perfectly tune the reactivity at boron, synthetic chemists have developed a wide array of substituents, from conventional boronates to MIDA esters.[3-7] Challenging metal-catalysed C-C couplings and orthogonal functionalizations were achieved by appropriately selecting the boron moieties.[7] For instance, one can hydrolyse boronate esters, using either acidic or basic conditions, or fluoro-derivatise them to yield organotrifluoroborates. In both cases, a nucleophilic attack at the boron vacancy is involved.[3,7] In the presence of 1,2 or 1,3-diols, boronic acids are in fast equilibrium at room temperature with boronate esters and water. This transesterification equilibrium can be shifted with the help of a desiccant or exploited in numerous molecular recognition or chemosensing applications[8] such as pH-dependent complexation of various carbohydrates[9] or smart drug delivery systems.[10] Following similar approaches, covalent dynamic crosslinking of organoboron polymers is receiving a growing interest in the context of materials with high mechanical performances and facilitated recycling or processing.[11,12]

Such crosslinks with externally adjustable dynamics (*e.g.* using temperature or light) are sought-after as they confer both the benefits of thermosets in conditions of slow dynamics (e.g. creep and stress-cracking resistance) and malleability, plasticity, weldability or recyclability in conditions of fast dynamics. A distinction can be made between dynamic polymer networks featuring a constant crosslink density with accelerated crosslink reshuffling upon heating, i.e. vitrimers,[13-15] and networks featuring both a decreased crosslink density and shorter crosslink-bond lifetimes upon heating or UV-irradiation[16], i.e. covalent adaptable networks (CANs). [17-20]

Based on both the transesterification equilibrium and the aforementioned reactivity at boron, CANs gels in toluene have been obtained by adding bis(boronate ester) crosslinkers in polycyclooctene-containing vicinal diol moieties. The exchanges can be tuned by strategically positioning secondary amines in the vicinity of the boron atoms, which greatly accelerates exchange dynamics.[21] Recently, Nicolaÿ, Leibler and coworkers disclosed fascinating covalent exchangeable vitrimer networks crosslinked by dynamic exchange of boronate ester linkages, albeit the actual exchange mechanism still remains unsolved.[22]

To the best of our knowledge, none of the dynamically crosslinked materials described so far reach the very high glass transition temperatures (T_g above 200°C) required for adhesives, protective coatings, low-wear or low-friction materials when exposed to high temperatures (contact with hot parts, composites for aerospace, electronics, bearings…). For such demanding applications, only a few thermoplastics constituted of very rigid segments, but with various degrees of solubility and processability are commercially available (e.g. polyaryletherketones, polyethersulfones,

polyaramides, polyetherimides or polybenzimidazoles).[23] Alternatively and historically, one can use non-reprocessable, very densely crosslinked thermosetting resins such as maleimide or phenolic formaldehyde, or specialty epoxies.[24]

All vitrimers disclosed so far have moderate crosslink densities, and exhibit therefore two clearly distinguishable relaxations: the conventional glass-to-rubber transition involving cooperative mobility at the scale of polymer segments and a second rubber-to-liquid transition related to crosslink exchanges and dynamic rearrangements of the network topology at the scale of the network mesh. Although the rubber-to-liquid transition can occur at very high temperatures in systems with sluggish exchange kinetics, the glass-to-rubber transition is contingent on the rigidity of the backbone in-between crosslinks and was not reported so far beyond 166°C.[25] Some CANs feature very rigid and densely crosslinked backbones, but their T_g is limited by de-crosslinking of the network at elevated temperatures: rigid furane-maleimide networks undergo a unique glass-to-liquid transition around 120°C.[17]

In this article we report that poly(4-vinylphenyl-pinacol-boronate ester) (PSBPin, Figure 1) exhibits a very high T_g up to 220°C. Although the bulky pinacol ester group is expected to reduce the chain mobility in comparison to polystyrene, the rigidity in the structure of the polymer and the polar interactions cannot account for such a high T_g. This compelled us to further explore the dynamics of this polymer linked to the reactivity of the pendant cyclic boronate. Herein we unveil a reaction mechanism involving dynamic and reversible ring openings of the cyclic boronate moieties at high temperatures.

1) Synthesis of PSBPin

The phenylboronate polymer was prepared *via* free radical polymerization of 4-vinylphenyl-pinacol-boronate ester.[1,26,27] The organoboron monomer was prepared *via* esterification with pinacol of the corresponding phenylboronic acid. It is important to note that the monomer always contains minute amounts of pinacol (<1 mol% by ^{1}H NMR), and we carried out polymerizations without further purification. This contamination will be discussed later on as a putative source of nucleophiles for initiating the ring opening mechanism. In order to minimize any residual functionality in the final polymer, we used benzoyl peroxide (BPO) as a nitrogen-free initiator (Figure 1 and Table 1; see sections 2, 3 and 4 of Supporting Information for further details & characterization). Careful optimization of polymerization temperatures, (non-transferable) solvents and initiator concentrations allowed us to obtain PSBPin with M_w as high as 200 kg.mol^{-1} (Table 1, Entry 5). This high-mass material was used for the rest of the study.

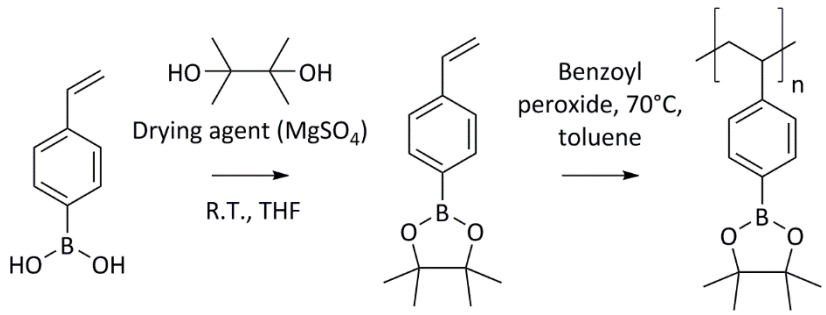

Figure 1. *Synthesis of poly(4-vinylphenyl-pinacol-boronate ester) (PSBPin).*

Table 1. *Synthesis optimization of poly(4-vinylphenylboronic pinacolate) (PSBPin). [1]Values determined by SEC-THF using PS standards and conventional calibration.*

Entry	Solvent	[Initiator] (mol eq.)	T (°C)	M_n (g/mol)[1]	M_w (g/mol)[1]
1	Toluene	0.01	80	25 000	39 000
2	Anisole	0.01	90	20 000	36 000
3	Dimethyl carbonate	0.01	80	12 000	17 000
4	Toluene	0.02	80	17 000	31 000
5	Toluene	0.02	70	42 000	230 000
6	Toluene	0.02	60	38 000	121 000
7	Toluene	0.02	80	25 000	44 000
8	Toluene	0.01	80	23 000	35 000

2) High T_g and Crosslinking

Freshly synthesized high-mass PSBPin was re-precipitated in pentane and thoroughly vacuum dried. Its thermal behaviour was first analysed by differential scanning calorimetry (DSC) (Figure 2). The thermogram showed upon first heating a shift in the baseline near 80°C, followed by a large endothermic event from 130 to 180°C and a second baseline shift near 220°C. Subsequent multiple cooling and heating cycles all revealed a single, well-defined, T_g with mid-point at 220°C. Thermogravimetric analysis (TGA) of the fresh sample did not reveal any significant weight loss in the 25-200°C range (Fig. 10 in SI), which ruled out a mere evaporation of plasticizers. We therefore surmised that the polymer had been chemically transformed, resulting in a very high T_g polymer after the initial heating step. Additional experiments ran in high-pressure sealed pans enabled to suppress most evaporation endotherms (Figures S7 & S8, SI). In such conditions, we observed a unique endotherm between 90 and 110°C. In this case the T_g is lowered to 160°C, even after multiple heating cycles.

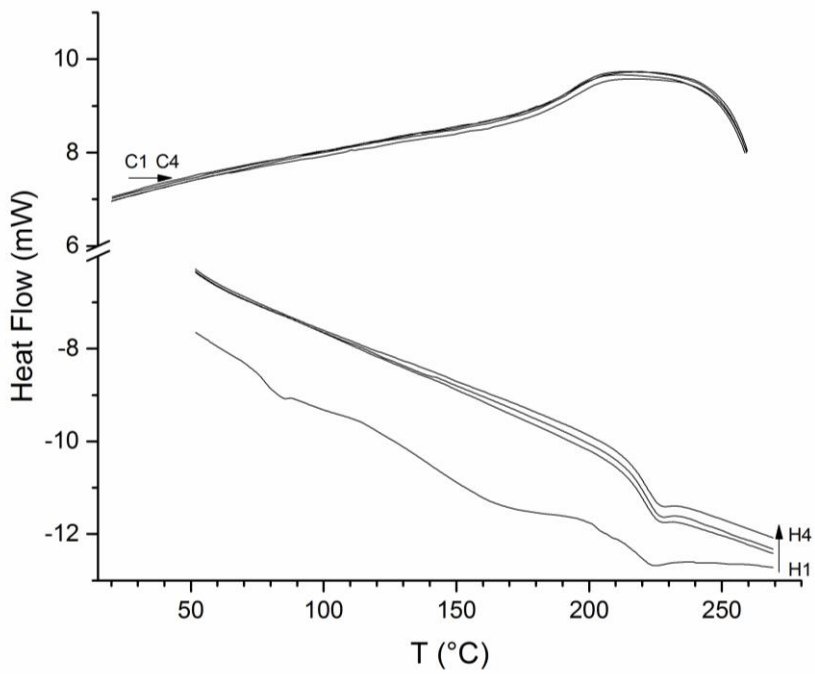

Figure 2. *DSC thermograms (Exo up) of PSBPin at 20 K/min. H1-4 and C1-4 are the successive heating and cooling ramps, respectively. Traces are cut at the beginning of each cooling and heating ramp for clarity.*

In order to better characterize the polymer after the heating step, we investigated its viscoelastic properties from 230 to 260°C by shear rheology, using small amplitude oscillations. Frequency-dependent storage and loss moduli at different temperatures were shifted by conventional time-temperature superposition in order to build a mastercurve using 230°C as reference temperature (Figure 3, right). The proximity to the glass transition was evidenced by the strong increase of G' and G" at high frequencies, while the upturn of G' at lower frequencies suggested the presence of entanglements or crosslinks. The dependency of the shift factors with temperature could not be fitted with the classical Williams-Landel-Ferry model (see Fig. S9 in SI), but followed instead an Arrhenius model with a very high activation energy, about 500 kJ/mol. These uncommon features suggest that the mechanical relaxations associated to the glass transition are not governed by cooperative segmental motions, but rather by chemical exchanges.[28] This polymer behaves therefore as a vitrimer with a unique glass-to-liquid transition. As lower frequencies could not be probed because of degradations starting to occur above 260°C, we rather chose to further study highly plasticized PSBPin as a 50 wt% solution in xylenes (bp ≈ 140°C). Monitoring in-situ the viscoelastic properties of this solution by small amplitude oscillations at 100°C (Figure 3, right) indicated initially a low-viscosity solution, followed by a strong increase in viscosity after about 10 h. Upon shearing with large deformations, the viscosity suddenly dropped but grew again within 4 h, showing this time a clear gelation with G'/G" crossover and an elastic modulus increasing up to 50 kPa.

The combination of DSC and rheology experiments thus indicates a dynamic crosslinking of PSBPin occurring very slowly in plasticized PSBPin at 100°C. The presence of an endothermic reaction in bulk PSBPin in the 130-180°C range points towards an analogous, faster crosslinking. However, complete characterization of the dynamic-crosslinking density is not possible as the transition associated to chemical exchanges appears coincident with the segmental glass transition.

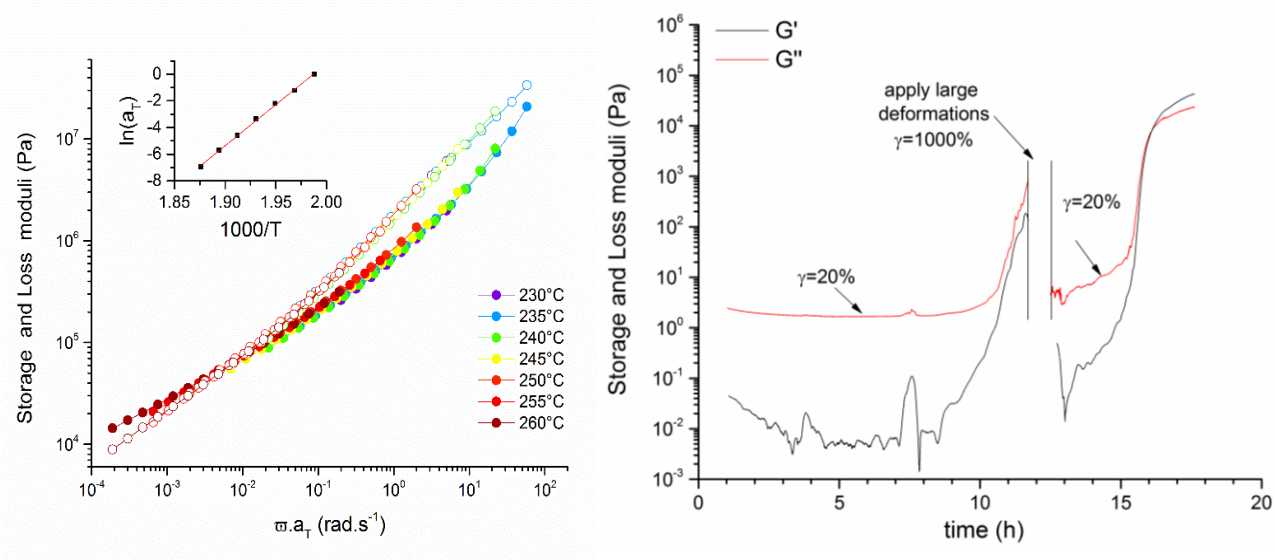

Figure 3. *Left: Master curve of dynamic storage and loss moduli of PSBPin in bulk, referenced at 230°C. Inset: Arrhenius-like dependency of the shift factors. Right: time monitoring of storage and loss moduli of PSBPin at 50 wt% in xylenes*

3) Solubility and Reversibility

While we have established that PSBPin undergoes apparent crosslinking upon heating up to 200°C at 20K/min, and even as concentrated solution over 10h at 100°C, we observed that the polymer could be completely resolubilised in most organic solvents after these heating treatments. Figure S14 in SI displays the SEC traces in toluene of fresh PSBPin and PSBPin taken from the DSC pan after multiple heating cycles. As no significant change occurred, it appears that the crosslinking reaction is dynamic, and can be fully reversed upon dilution (see Fig. 15 in SI).

4) Spectroscopic evidence of the Reaction

In order to better understand the reaction involved in the dynamic crosslinking, we carried out temperature-dependent FTIR measurements under inert atmosphere from 25 to 250°C (10°C increments per hour) using a diffuse reflectance cell. The fresh PSBPin powder was used directly rather than samples obtained by hot or cold pressing. A few small but noticeable variations appeared in the 100-170°C range in the spectra (see Figures S17 & S18 in SI). Among them, two main changes raised our attention: a shouldering around 1370 cm^{-1} and a band shift from ca. 1170 to 1160 cm^{-1}. These vibration modes involve torsions/elongations of the O–B–O as well as C–O bonds of the pinacol motif as assigned by frequency calculations performed at the DFT level (M06/def2TZVP) on model pinacol phenyl boronate (see SI). *This drove us to hypothesize a ring opening of the boronate cycles*.

Solid-state boron NMR spectroscopy was therefore used to detect differences in the environment of the boron atoms of PSBPin before and after heating. ^{11}B ss-NMR is not straightforward because of the quadrupolar nature of the ^{11}B nucleus (spin 3/2). Thus, when comparing signals, one should not conclude immediately from the maximum of intensity of the observable massif, but instead derive the isotropic chemical shift (δ_{iso}), the ηQ values (related to the mobility of the corresponding boron atom) and observe the relative asymmetries/anisotropies of the signals. In our case, when superimposed, the two signal envelopes were distinct, suggesting an altered boron environment once PSBPin was exposed to high temperatures (Figure 4). To evaluate whether only one or several types of boron chemical environments were present, we used simulations from the "dmfit" program, which was specifically developed to account for quadrupolar couplings.[29] One type of boron was sufficient to perfectly fit the experimental signal before heating. Conversely, two types of boron were necessary to achieve perfect match between simulation and experimental spectrum when fitting the signal after heating. Furthermore, the simulations established that the new type of Boron formed after heating (~16 mol%) had more symmetrical features, in particular quadrupolar couplings with lower ηQ value (see Figure 4), and a different δ_{iso} of 32.5 ppm. This is indicative of an enhanced mobility and is compatible with boronate esters with pendant or intermolecular bridging pinacolates. The main environment was common to the samples before and after heating, with a δ_{iso} of 30.5 ppm before (~30 after) and similar relatively high ηQ values (0.71 and 0.63, respectively) thus indicative of a constrained geometry. It was attributed to native pinacol phenyl boronate cyclic species. The slight differences in δ_{iso} might come from residual solvent evaporation (toluene traces or adsorbed moisture no longer present after heating for 4h at 200°C). The newly formed type of boron displays an enhanced mobility, as can be expected when the ring opens. Therefore, ^{11}B ss-NMR corroborates our hypothesis of ring opening of cyclic pinacol boronates.

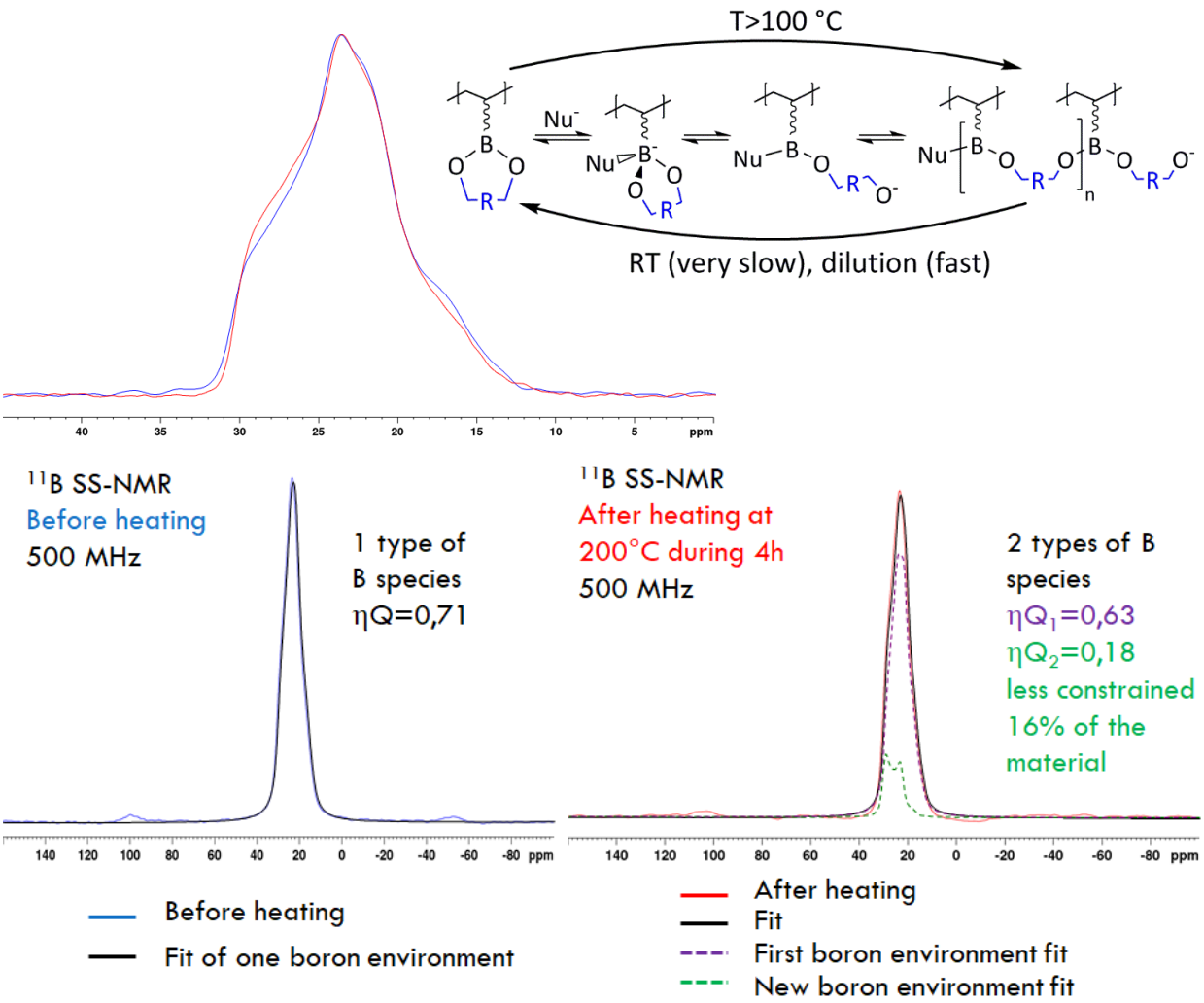

Figure 4. *Solid-state ^{11}B NMR study of poly(4-vinylphenylboronic acid, pinacol ester) (PSBPin). (a) Superimposition of ^{11}B NMR signal of PSBPin before and after heating at 200°C for 4h. (b) ^{11}B NMR spectrum of native PDBPin and corresponding fit, (b) ^{11}B NMR spectrum of PSBPin after heating at 200°C for 4 hours and corresponding fits. I am not to sure that the the sp3 boronate is a stable intermediate in this case.*

5) Putative Mechanism

Taking into account the body of evidence obtained so far, we suggest that the ring opening of the boronates releases a free pinacolate moiety that can further reach neighbouring boron atoms thus acting as a rigid crosslink between PSBPin chains. This leads to a strong decrease in the chain mobility, consistently with the very high T_g observed. DSC and rheology data corroborate this ring opening occurring at high temperatures (130-180°C) and the subsequent dynamic character of the crosslinks formed.

Regarding the initiation of the ring opening, the involvement of a nucleophile and the assistance by an acid seem compulsory: adventitious water or the residual pinacol molecules

remaining from the synthesis could fill both roles. The nucleophilic attack at boron and the subsequent ring opening would lead to singly-attached pinacol group readily available to initiate ring opening of a proximal pinacol boronate, ultimately triggering bridge formation. We resorted to computational mechanistic investigation performed at the DFT level in order to assess the enthalpy of ring opening of these pinacol boronates (see details in SI). In this investigation, PSBPin units have been represented by phenyl pinacol boronate and a water molecule has been used as prototype nucleophile. At room temperature, the interaction of H_2O with a pinacol oxygen atom *via* H-bonding is exothermic by 4.4 kcal.mol^{-1} at 293 K. This adduct will be taken as the energy reference hereafter. From this adduct, the subsequent ring opening to yield a singly-attached pinacol substituted boronic acid is endothermic by 3 kcal.mol^{-1} (see Fig. S16, SI). In Gibbs energy, the reaction is endergonic by 4.0 kcal.mol^{-1}. Consequently, the ring opening is slightly entropically favoured but requires heating to circumvent the endothermicity of the reaction. This thermodynamic trend is consistent both with the net endothermic reaction measured by DSC (see Fig. 8, see SI) and with crosslinking observed above 100°C. We infer that this system, with a peculiar thermodynamic balance between the enthalpic and entropic contributions, is reminiscent of floor-temperature polymerizations already demonstrated in several low-strained cyclic monomers.[30,31] Kinetically, the enthalpy (resp. Gibbs energy) barriers corresponding to ring opening is calculated at 27 (resp. 30) kcal.mol^{-1} above the water adduct, with a clear pyramidalisation induced by H_2O nucleophilic attack at B through O. Interestingly, the energy barrier corresponding to a direct metathesis has been estimated to 70 kcal.mol^{-1} relative to the free pinacolboronate. This mechanism can thus be confidently ruled out.

Even though the overall entropy of the system would likely limit the extent of oligomerisation, bridging between boron atoms appears sufficient to trigger dense crosslinking in these highly functional polymers at high temperature. Furthermore, the de-crosslinking induced at high dilutions is likely entropically-driven by the formation of the more favoured intramolecular 5-membered cycle in the presence of a high concentration of solvent molecules. This de-crosslinking should also be favoured at low T°C but is most probably kinetically frozen by the glass transition in PSBPin.

6) Complementary experiments on model compounds

In order to verify this mechanism, we performed double-tagging experiments. If the dynamic character of the ring-opening oligomerization is effectively due to the living character of the pendant pinacolate groups, we should not only observe oligomerisation and depolymerisation of the model molecules, but also backbiting or chain shuffling that could result in more complex rearrangements and effective exchange of substituents between boronate esters (Figure 5). These exchanges should be evidenced by double tagging: we therefore prepared two phenylboronate esters **A** and **B** (Figure 5, and section 5 of SI). **A** has a phenyl ring and its diol component is 1,2-ethanediol while **B** has a fluorine tag on the phenyl part and pinacol as its diol. The fluorine substituent enables straightforward quantification of any diol exchanged by ^{19}F NMR, while only marginally affecting the intrinsic reactivity at the boron atom. The boronates **A** and **B** were mixed without additional solvent in a NMR tube and heated at 100°C. Periodically, the NMR tube was cooled at room temperature, equipped with an insert filled with Toluene-*d8* to lock the NMR apparatus and analysed with ^{19}F NMR. While only A could initially be observed, a new species appeared with time that was attributed to the F-tagged phenyl boronate bearing an ethylene glycol group (**C**, see Figure 5). The attribution of the new ^{19}F NMR signal to **C** was confirmed by separately synthesising the 4-fluoro-phenyl boronate of ethylene glycol (see SI, Fig. S21 & S22). Integration of the signals corresponding to **A** and **C** at –107.8 ppm and –108.2 ppm, respectively, showed that a nearly 1:1 equilibrium was reached after 50 h.

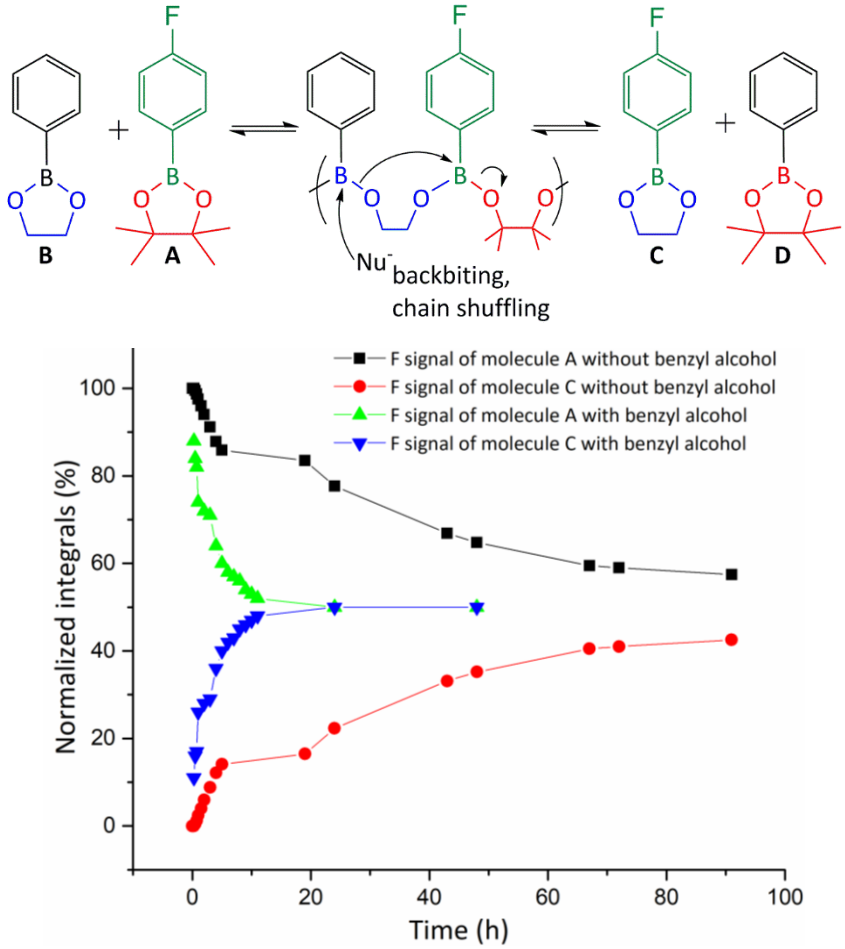

Figure 5. *Double-tagging experiments using ^{19}F NMR spectroscopy.*

In order to support our hypothesis that the crosslinks were initiated by the adventitious nucleophiles still present in the sample, we added 50 mol% of benzyl alcohol - a non-volatile nucleophile - in the initial mixture. ^{19}F NMR monitoring at 100°C showed a much faster exchange rate, as the **A** / **C** 1:1 equilibrium was reached within 12h. In addition, smaller new signals could be observed on the ^{19}F NMR spectra, which we believe are those of the benzyl-alcohol derived phenyl boronates and several other products/intermediates of the exchange reaction (*e. g.* the tetragonal intermediates), which was partially confirmed by ^{19}F DOSY NMR experiments.(see section 5 in SI, Figures S19 to S24)

Dynamic gelation of a 50 wt% concentrated PSBPin solution in toluene in presence of 2 mol% of benzyl alcohol is illustrated in Figure 6 (and Fig. S15 in the SI). After heating the viscous solution for 72h at 100°C, gelation was observed. Upon cooling to room temperature and further addition of toluene (the final concentration is 25 wt% PSBPin), immediate swelling was visible. After 2 min, the gel was fully broken and a low-viscosity solution was obtained.

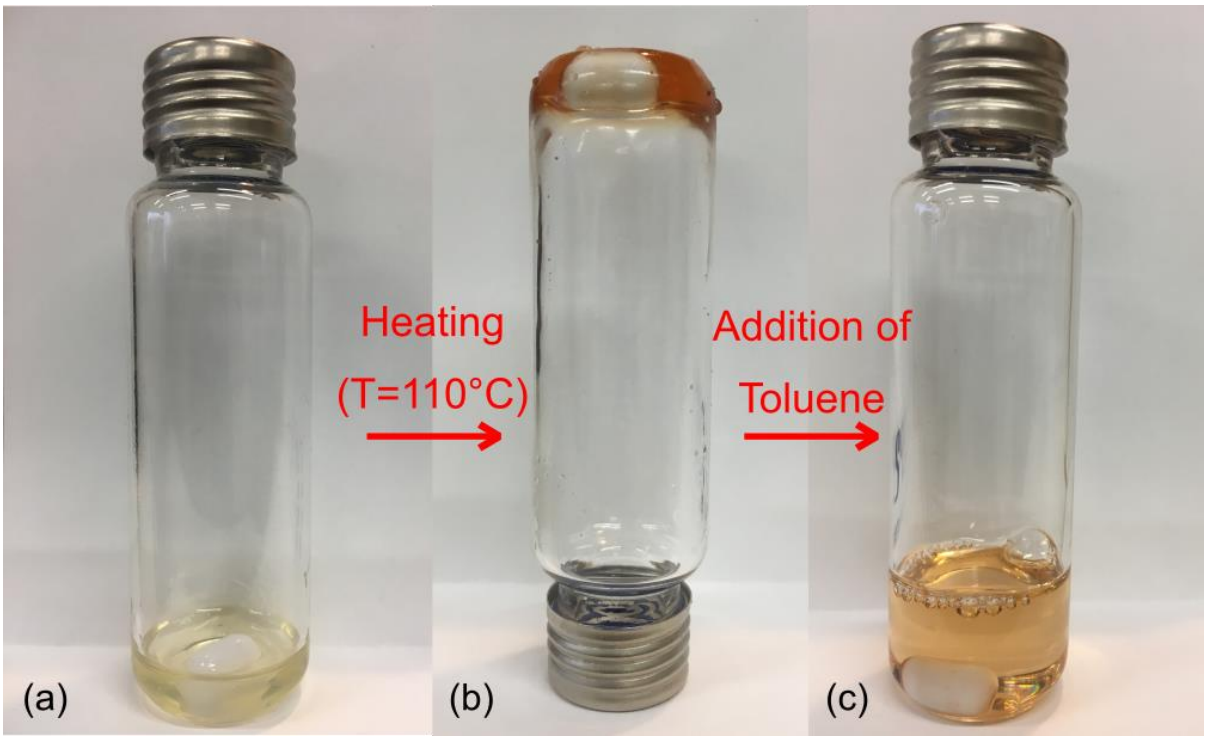

Figure 6. *Macroscopic observations of the reversible crosslinking of an originally 50 wt% concentrated PSBPin solution in toluene.*

7) Conclusion

We have demonstrated through a variety of thermomechanical and spectroscopic techniques (DSC, rheology, FTIR, ^{11}B ss-NMR) that above 100°C boronic ester ring-opening occurs in poly(4-vinylphenylboronic pinacolate)s, leading to interchain bridging between boron moieties and high-Tg (up to 220°C) polymer networks. Direct exchange of 1,2-diol substituents was evidenced on model compounds by ^{19}F NMR spectroscopy, and confirms the dynamic character of the ring opening and the importance of nucleophilic assistance to trigger it. This phenomenon appears to be reversible by dilution in apolar solvents. The peculiar thermodynamics of this ring opening/closing sequence, supported by DFT calculations, favour depolymerisation at room temperature and oligomerisation at high temperatures. The very fact that bridging between boron atoms lead to high glass transition temperatures in our system and subsequently froze the depolymerisation kinetics was critical in evidencing these dynamic crosslinking phenomena. When comparing our system to vitrimers and CANs, that have either constant crosslinking densities or decreasing crosslinking densities with temperature, it is exciting to note that polymers bearing cyclic boronate esters may constitute the first example of a distinct class of dynamic networks, with a crosslinking density increasing with temperature, at least within a defined temperature range.

Acknowledgements

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Author contributions

JB, FB, EL, DM and JR designed and analysed the experiments. JB carried out the experiments. MH carried out solid state NMR measurements. FC helped analysing and designing DSC experiments. LP and FB conducted DFT calculations. JB, EL, DM and JR wrote the manuscript.

Competing interests

All authors declare no competing interests.

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